

StatMech questions

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1.1 What is a canonical ensemble

Canonical, or NVT ensemble is set of N particles, in a given volume with a given temperature. Canonical ensemble describes a equilibrium system in the box with constant volume, where the temperature is constant because of interection with an environment (bath).

1.2 What is a partition function for canonical ensemble

Partition function for canonical ensemble is defined by the expression

$$Z_N = \frac{1}{(2\pi\hbar)^{3N}} \cdot \frac{1}{N!} \int e^{-\beta\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)} d\mathbf{r}^N d\mathbf{p}^N \quad (1)$$

where

N is number of particles

\hbar is a Planck constant

$\beta = \frac{1}{k_B T}$, T - temperature, k_B - Boltzman constant

$\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N)$ is the Hamiltonian

$\mathbf{r}^N = \mathbf{r}_1, \dots, \mathbf{r}_N$ are coordinates of particles

$\mathbf{p}^N = \mathbf{p}_1, \dots, \mathbf{p}_N$ are momenta of particles

1.3 What is a conficurationl integral

Configuration integral is defined by formula

$$Q_N = \int e^{-\beta U(\mathbf{r}^N)} d\mathbf{r}^N \quad (2)$$

where

N is number of particles

$\beta = \frac{1}{k_B T}$, T - temperature, k_B - Boltzman constant

$U(\mathbf{r}^N)$ is potential energy

$\mathbf{r}^N = \mathbf{r}_1, \dots, \mathbf{r}_N$ are coordinates of particles

1.4 What is de Broigle length

De Broigle wavelength is the length of wave associated with a moving quantum particle:

$$\lambda = \frac{2\pi\hbar}{p} \quad (3)$$

where

\hbar is a Planck constant

p is momenta of a particle

If momenta of the particle has Maxwell's distribution, the mean momenta in some direction of particle is

$$\bar{p} = \int_{-\infty}^{+\infty} e^{-\frac{1}{k_B T} \frac{p_x^2}{2m}} dx = \sqrt{2\pi m k_B T} \quad (4)$$

Putting it to the general definition (3) we obtain *Thermal de Broglie wavelength*

$$\Lambda = \sqrt{\frac{2\pi\hbar^2}{m k_B T}} \quad (5)$$

1.5 How does partitition function relates to conf. integral and de Brougle length

The Hamiltonian is composed of kinetic and potential energy terms:

$$\mathcal{H}(\mathbf{r}^N, \mathbf{p}^N) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m} + U(\mathbf{r}^N, \mathbf{p}^N) \quad (6)$$

where

N is number of particles

$\mathbf{r}^N = \mathbf{r}_1, \dots, \mathbf{r}_N$ are coordinates of particles

$\mathbf{p}^N = \mathbf{p}_1, \dots, \mathbf{p}_N$ are momenta of particles

$p_i = (p_x, p_y, p_z)$ is momenta of i -th particle

m is the mass of the particle

Putting (6) to the partition function (1) we may separate integrals by coordinates and momenta:

$$\begin{aligned} Z_N &= \frac{1}{(2\pi\hbar)^{3N}} \cdot \frac{1}{N!} \int e^{-\beta \sum \frac{\mathbf{p}_i^2}{2m}} d\mathbf{p}^N \int e^{-\beta U(\mathbf{r}^N, \mathbf{p}^N)} d\mathbf{r}^N \\ &= \frac{1}{(2\pi\hbar)^{3N}} \cdot \frac{1}{N!} \left(\int e^{-\beta \frac{\mathbf{p}^2}{2m}} d\mathbf{p} \right)^N Q_N \end{aligned} \quad (7)$$

where

Q_N is configurational integral (2)

\mathbf{p} is momenta of a single particle

$\beta = \frac{1}{k_B T}$, T - temperature, k_B - Boltzman constant

m is the mass of the particle

The integral over momenta in (7) can be calculated directly:

$$\int e^{-\beta \frac{\mathbf{p}^2}{2m}} d\mathbf{p} = \left(\int_{-\infty}^{+\infty} e^{-\frac{p_x^2}{2mk_B T}} dp_x \right)^3 = (2\pi m k_B T)^{\frac{3}{2}} \quad (8)$$

Putting this to (7) we have:

$$Z_N = \frac{1}{N!} \cdot \left(\frac{\sqrt{2\pi m k_B T}}{2\pi\hbar} \right)^{3N} Q_N = \frac{1}{N! \Lambda^{3N}} Q_N \quad (9)$$

This is the relation between the Partition function (1), Configuration integral (2) and Thermal de Broigle wavelength (5)

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2.1 What is a free energy

Free energy of the canonical (NVT) ensemble (*Helmholtz Free Energy*) is:

$$\mathcal{F} = -k_B T \log Z_N = \bar{E} - TS \quad (10)$$

where

Z_N is Partition function (1)

\bar{E} is a mean energy

T is a temperatre

S is Entropy of the system

Gibbs Free Energy is defined for the NPT ensemble:

$$\mathcal{F} = \bar{E} + PV - TS = H - TS \quad (11)$$

where

P is preasure

T is temperature

S is Entropy $H = \bar{E} + PV$ is Enthalpy

The defferential of Free energy is:

$$d\mathcal{F} = -SdT - PdV + \mu dN \quad (12)$$

where

S is Entropy P is presure μ is chemical potential

Considering (10) we have:

$$d\bar{E} - TdS - SdT = -SdT - PdV + \mu dN \quad (13)$$

or

$$d\bar{E} = TdS - PdV + \mu dN \quad (14)$$

2.2 What is entropy

Entropy is proportional to the logarithm of statistical weight of the macroscopic state, which show how much different microscopic states corresponds to macroscopic ones. Entropy of the system can be obtained by formula:

$$S = -k_B \overline{\log (2\pi\hbar)^{3N} P(\mathbf{r}^N, \mathbf{p}^N)} \quad (15)$$

where $P(\mathbf{r}^N, \mathbf{p}^N)$ is the probability to find system at the point $(\mathbf{r}^N, \mathbf{p}^N)$ in the phase space and the line over the right side means the mean over the phase space:

$$S = -\frac{k_B}{N!} \int P(\mathbf{r}^N, \mathbf{p}^N) \log \left((2\pi\hbar)^{3N} P(\mathbf{r}^N, \mathbf{p}^N) \right) d\mathbf{r}^N d\mathbf{p}^N \quad (16)$$

As well, it can be found from the (12) as the partial derevative of Free Energy:

$$S = -\frac{\partial \mathcal{F}}{\partial T} \quad (17)$$

2.3 What is enthalpy

Enthalpy can be found from (12) by the formula:

$$H = \bar{E} + PV \quad (18)$$

where \bar{E} is the mean energy

P is pressure

V is volume

2.4 What is a chemical potential

Chemical potential can be found from (12) as the partial derivative of the free Energy:

$$\mu = \frac{\partial \mathcal{F}}{\partial N} \quad (19)$$

where N is the number of particles

It shows how much changes the free energy with the adding new particles to the system.

2.5 Write S, H, μ , partition function for ideal gas

In the case of ideal gas potential energy is zero. Then, configuration integral (2) is

$$Q_N = \int e^0 d\mathbf{r}^N = V^N \quad (20)$$

Using expression (9) we find the partition function of ideal gas:

$$Z_N = \frac{V^N}{N! \Lambda^{3N}} \quad (21)$$

Putting it to the expression (10) we found the Free energy:

$$\mathcal{F} = -k_B \log \left(\frac{V^N}{\Lambda^{3N} N!} \right) = -Nk_B T \log V + k_B T \log N! + Nk_B T \log \Lambda^3 \quad (22)$$

Using that $\log N! \approx N \log \frac{N}{e}$ we obtain:

$$\mathcal{F} = Nk_B T \log \left(\frac{N}{V} \cdot \frac{\Lambda^3}{e} \right) \quad (23)$$

We may obtain entropy by taking partial derivative of Free Energy of ideal gas, using the formula (17). However, during taking derivative one should remember that in formula (23) Thermal de Broglie wavelength Λ is defined by (5) and depends on the temperature.

We have:

$$\begin{aligned} S &= -Nk_B T \log \frac{N\Lambda^3}{Ve} - Nk_B T \frac{\partial}{\partial T} \left(\log \frac{N}{Ve} \left(\frac{2\pi\hbar^2}{mk_B} \right)^{\frac{3}{2}} - \frac{3}{2} \log T \right) \\ &= Nk_B \left(\frac{3}{2} - \log \frac{N\Lambda^3}{Ve} \right) = Nk_B \left(\frac{5}{2} - \log \frac{N\Lambda^3}{V} \right) \end{aligned} \quad (24)$$

We may obtain chemical potential by derivating Free Energy (23) over number of particles N:

$$\mu = k_B T \log \frac{N\Lambda^3}{V} \quad (25)$$

As it is seen from (12), pressure can be found by the formula:

$$P = -\frac{\partial \mathcal{F}}{\partial V} \quad (26)$$

Taking derivative from (23) we have expression for pressure of ideal gas:

$$P = \frac{Nk_B T}{V} \quad (27)$$

or

$$PV = Nk_B T \quad (28)$$

3 Dependence between free energy (preassure, chemical potential, compressibility) and n

n is a *Number Density*: Number of particles N in the volume V

$$n = \frac{N}{V} \quad (29)$$

The classical approximation is valid, when $n \ll \Lambda^3$

Putting (29) to the (23) we obtain dependence between free energy and n:

$$\mathcal{F} = nV k_B T (\log n \Lambda^3 - 1) \quad (30)$$

This dependance can be illustrated on the plot:

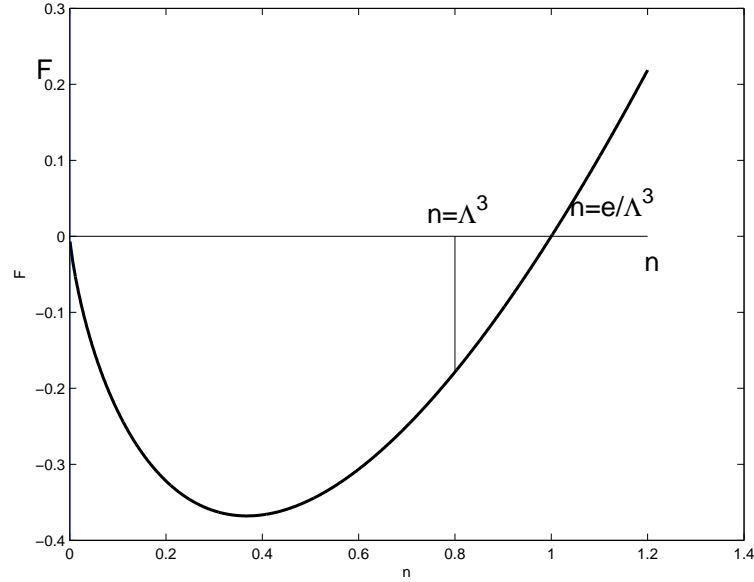


Figure 1: Dependence of free energy on number density. When $n = \Lambda^3$ the classical approximation becomes invalid

Expression for the chemical potential is obtained from (25):

$$\mu = k_B T \log n \Lambda^3 \quad (31)$$

It is just logarithmical dependence. When $n \rightarrow 0$ chemical potential tends to infinity: $\mu \rightarrow -\infty$. It crosses the zero when $n = \frac{e}{\Lambda^3}$

As it is seen from (27) preassure is linearly proportional to the number density:

$$P = nk_B T \quad (32)$$

and the temperature is inverse proportional to the number density:

$$T = \frac{P}{nk_B} \quad (33)$$

Isothermal compressibility is defined by the formula:

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (34)$$

Using relation (28) we found:

$$\kappa = \frac{Nk_B T}{V P^2} = \frac{nk_B T}{P^2} \quad (35)$$

Considering the dependency of preassure on the number density (32) we have:

$$\kappa = \frac{1}{nk_B T} \quad (36)$$

4 Grand Canonical Ensemble

4.1

Grand Canonical, or μVT ensemble is set of particles, in a given volume with a given temperature. Number of particles can change, however, chemical potential μ is also given. In this case energy of ensemble E_N depends on the number of particles. As well, probability to find N particles at the point $(\mathbf{r}^N, \mathbf{p}^N)$ is now considered as a fuction of number of particles:

$$P^{(N)}(\mathbf{r}^N, \mathbf{p}^N) \equiv P(N, \mathbf{r}^N, \mathbf{p}^N) \quad (37)$$

4.2 Grand Potential

In the case of Grand Canonical ensemble, probability density function (37) is:

$$P^{(N)} = A e^{\beta(\mu N - E_N)} \quad (38)$$

Putting this to the expression for an entropy (15), we have:

$$S = -k_B \log((2\pi\hbar)^{3N} A) - \frac{\mu \bar{N}}{T} + \frac{\bar{E}}{T} \quad (39)$$

We can donote

$$\Omega \equiv k_B T \log((2\pi\hbar)^{3N} A) = \bar{E} - TS - \mu \bar{N} \quad (40)$$

This is *Grand Potential* of the body.

The differential of a Grand Potential is:

$$d\Omega = -SdT - PdV - \bar{N}d\mu \quad (41)$$

Which yields such expressions for thermodynamic variables:

$$P = - \left(\frac{\partial \Omega}{\partial V} \right)_{T, \mu} \quad (42)$$

$$S = - \left(\frac{\partial \Omega}{\partial T} \right)_{V, \mu} \quad (43)$$

$$\bar{N} = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{V, T} \quad (44)$$

4.3 Activity

From (40) we may find the constant A :

$$A = \frac{e^{\beta \Omega}}{(2\pi\hbar)^{3N}} \quad (45)$$

Putting it to the formula (38) we have:

$$P^{(N)}(\mathbf{r}^N, \mathbf{p}^N) = \frac{1}{(2\pi\hbar)^{3N}} e^{\beta \Omega} \lambda^N e^{-\beta E_N(\mathbf{r}^N, \mathbf{p}^N)} \quad (46)$$

Where λ is *activity*:

$$\lambda = e^{\beta \mu} \quad (47)$$

4.4 Grand Partition Function

Probability to find N particles in the system is integral over the phase space of probabilities of microstates (46):

$$P(N) = \frac{1}{N!} \int P^{(N)}(\mathbf{r}^N, \mathbf{p}^N) d\mathbf{r}^N d\mathbf{p}^N = e^{\beta \Omega} \lambda^N Z_N \quad (48)$$

where Z_N is the partition function of canonical ensemble with N particles (1).

Probability to find system in one of states in unity. So we may write the normalizing condition:

$$1 = \sum_N P(N) = e^{\beta \Omega} \sum_N \lambda^N Z_N \quad (49)$$

From this expression we can find the formula for the Grand Potential:

$$\Omega = -k_B T \log \Xi \quad (50)$$

where Ξ is a *Grand Partition Function*

$$\Xi = \sum_N \lambda^N Z_N \quad (51)$$

4.5 $\Xi, \Omega, P, S, \bar{N}$ for the ideal gas

If we substitute expression (21) to the (51) we obtain the Grand Partition function of ideal gas:

$$\Xi = \sum_N \frac{1}{N!} \left(\frac{\lambda V}{\Lambda^3} \right)^N \quad (52)$$

One may see, that this is Teilor expansion for the exponential function:

$$\Xi = e^{\frac{\lambda V}{\Lambda^3}} \quad (53)$$

Putting this expression to the (50) we found Grand Potential of ideal gas:

$$\Omega = -k_B T e^{\beta \mu} \frac{V}{\Lambda^3} \quad (54)$$

This equation might be rewritten as an explicit function of macroscopic parameters μ, V, T by substituting expressions (5) and $\beta = \frac{1}{k_B T}$:

$$\Omega = - \left(\frac{m}{2\pi\hbar^2} \right)^{\frac{3}{2}} e^{\frac{\mu}{k_B T}} V (k_B T)^{\frac{5}{2}} \quad (55)$$

Preassure might be found from (54) by derivating over volume (42)

$$P = e^{\beta \mu} \frac{k_B T}{\Lambda^3} = \left(\frac{m}{2\pi\hbar^2} \right)^{\frac{3}{2}} e^{\frac{\mu}{k_B T}} (k_B T)^{\frac{5}{2}} \quad (56)$$

Entropy of ideal gas is partial derivative of (55) by T (43)

$$\begin{aligned} S &= -\frac{\partial}{\partial T} \left(- \left(\frac{m}{2\pi\hbar^2} \right)^{\frac{3}{2}} e^{\frac{\mu}{k_B T}} V (k_B T)^{\frac{5}{2}} \right) = \left(\frac{m}{2\pi\hbar^2} \right)^{\frac{3}{2}} V \left(-\frac{\mu}{k_B T^2} e^{\frac{\mu}{k_B T}} (k_B T)^{\frac{5}{2}} + \frac{5}{2} e^{\frac{\mu}{k_B T}} (k_B T)^{\frac{3}{2}} \right) \\ &= (k_B T)^{\frac{3}{2}} e^{\beta \mu} V \left(\frac{5}{2} - \frac{\mu}{T} \right) \end{aligned} \quad (57)$$

Mean number of particles can be found from (54) by (44):

$$\bar{N} = e^{\beta \mu} \frac{V}{\Lambda^3} = \left(\frac{m}{2\pi\hbar^2} \right)^{\frac{3}{2}} e^{\frac{\mu}{k_B T}} V (k_B T)^{\frac{3}{2}} \quad (58)$$